Dehalogenation of Organic Compounds by Reductive Radicals

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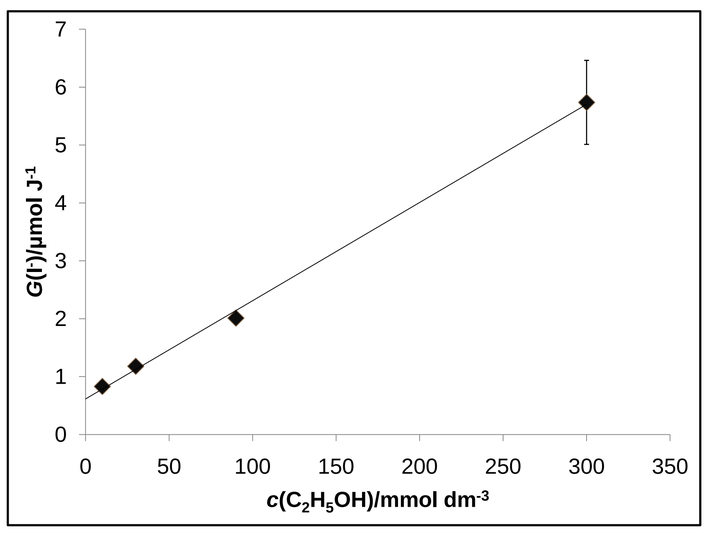
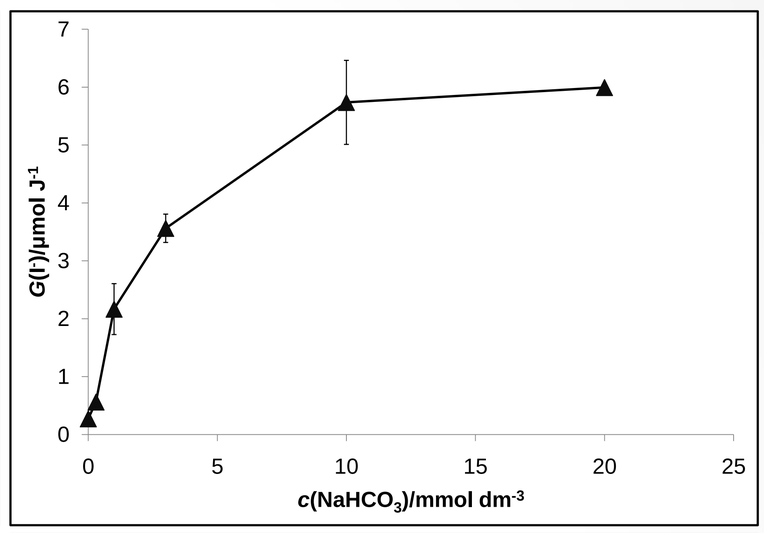
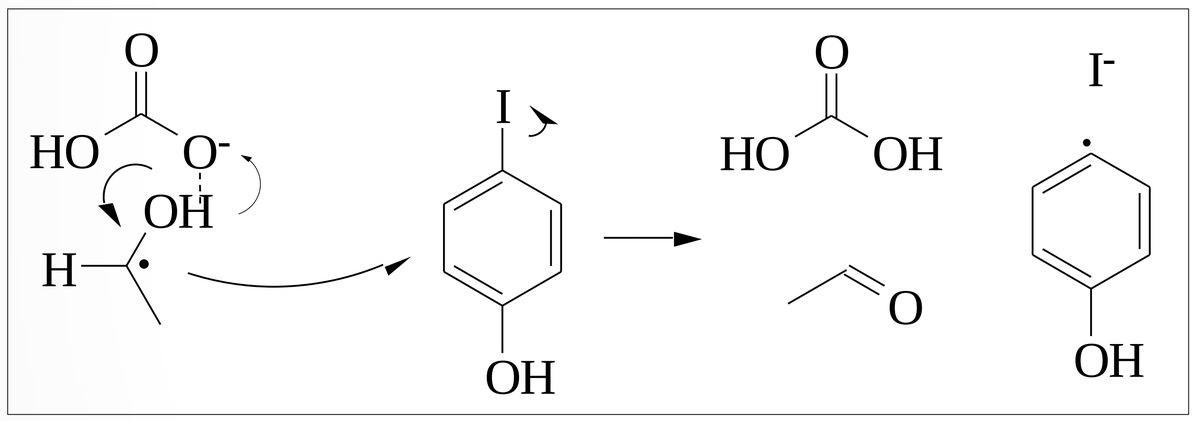
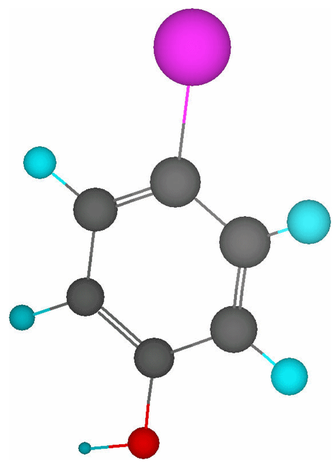
Halogenated aromatic compounds are common toxic pollutants of industrial and communal waters. Usual methods used for their decomposition are radical-based, primarily with hydroxyl radical ($^{\bullet}OH$). This radical is highly reactive with all agents present in water so overall yields are very low. Therefore, it is interesting to find out other potentially useful radicals for radiolysis of chloro-, bromo-, and iodophenols, halogenated aliphatic compounds and 5-bromouracil. Carbon-centred radicals, $^{\bullet}CH(CH_3)OH$, $^{\bullet}CH_2OH$, and $^{\bullet}CO_2^-$, in air-free aqueous solutions in the presence of ethanol, methanol or sodium formate as precursors of reductive organic radicals have been employed.









The presence of sodium hydrogen carbonate and ammonium acetate significantly influences reduction power of carbon-centred radicals (except $^{\bullet}CO_2^-$), while presence of stronger base, potassium hydrogen phosphate, does not improve reduction power of those radicals which is otherwise insufficient for reduction. In systems where reduction is operative, dehalogenation has been observed to occur by a chain process. Additionally, complex between base and reductive radical is formed in case of $^{\bullet}CH(CH_3)OH$ and $^{\bullet}CH_2OH$. Mechanisms of the abovementioned reduction reactions, simple electron transfer mechanism for $^{\bullet}CO_2^-$ and proton-coupled electron transfer for $^{\bullet}CH(CH_3)OH$ and $^{\bullet}CH_2OH$, have been investigated. System with the concentration of $NaHCO_3$ of 10 mmol/dm^3 gives the optimal outcome, i.e. the highest yield of halide ions with as low concentration of other components as possible but even better rate constants have been achieved with $^{\bullet}CO_2^-$ (for one to two orders of magnitude). Equilibrium constants of complexes observed in this work has been estimated to be almost the same.

Generation of radicals has been induced by γ-radiolysis (^{60}Co) of aqueous solutions in the presence of various organic compounds. Primary water radicals:

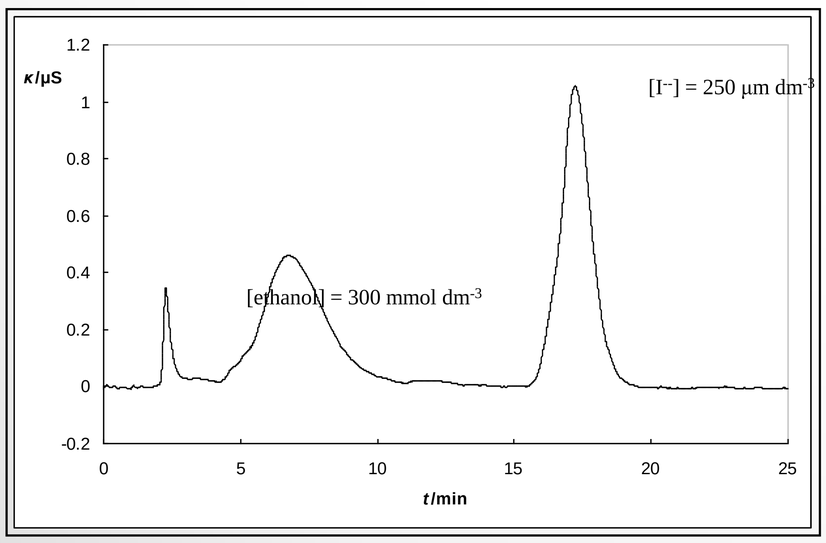
$H_2O \quad \sim\sim\sim\rightarrow \quad e_{aq}^-$, $^{\bullet}OH$, $^{\bullet}H$

in the yields of G = 0.3; 0.3; 0.06 μmol J^{-1} have participated in following chain reactions:

$e_{aq}^- + ArHal \rightarrow Hal^- + Ar^{\bullet}$

$^{\bullet}OH$ / $^{\bullet}H + RH \rightarrow H_2O/H_2 + R^{\bullet}$

Concentrations of halogenide ions have been determined by the means of ion chromatography (on Dionex DX-120, anionic columns AS14 and AS17, eluents 1 mmol dm^{-3} $NaHCO_3$: 3.5 mmol dm^{-3} Na_2CO_3 or 15 mmol dm^{-3} of NaOH). Chromatogram of one sample has been shown on the picture (air-free, neutral solution of 4-I-C_6H_4OH (c = 1 mmol dm^{-3}), ethanol (c = 0.3 mol dm^{-3}), $NaHCO_3$ (c = 10 mmol dm^{-3}), dose of radiation D = 40.2 Gy).



B. Matasović, M. Bonifačić, Reductive Halogen Elimination from Phenol by Organic Radicals in Aqueous Solutions; Chain Reaction Induced by Proton-Coupled Electron Transfer, J. Phys. Chem. A, **111** (2007) 8622 – 8628.

B. Matasović, M. Bonifačić, Reductive Dehalogenation of 5-Bromouracil by Aliphatic Organic Radicals in Aqueous Solutions; Electron Transfer and Proton-Coupled Electron Transfer Mechanisms, Rad. Phys. Chem., **80** (2011) 750 – 754.

system	k/dm^3 mol^{-1} s^{-1}	pH	R$^{\bullet}$	R'H
iodoethane + 10 mmol dm^{-3} hydrogen carbonate + methanol	1.8 ± 0.1	7	$^{\bullet}C_2H_5$	CH_3OH
iodoethane + 1 mmol dm^{-3} hydrogen carbonate + ethanol	2.9 ± 0.2	7	$^{\bullet}C_2H_5$	C_2H_5OH
iodoethane + 3 mmol dm^{-3} hydrogen carbonate + ethanol	4.7 ± 0.4	7	$^{\bullet}C_2H_5$	C_2H_5OH
iodoethane + 10 mmol dm^{-3} hydrogen carbonate + ethanol	7.2 ± 0.9	7	$^{\bullet}C_2H_5$	C_2H_5OH
iodethanoate + ethanol	60 ± 10	7	$^{\bullet}CH_2COO^-$	C_2H_5OH
iodethanoate + methanol	20 ± 2	7	$^{\bullet}CH_2COO^-$	CH_3OH
iodethanoate + methanoate	519 ± 4	7	$^{\bullet}CH_2COO^-$	$HCOO^-$
bromouracil + 10 mmol dm^{-3} hydrogen carbonate + ethanol	27 ± 7	7	$^{\bullet}C_4H_3N_2O_2$	C_2H_5OH
bromouracil + 10 mmol dm^{-3} hydrogen phosphate + ethanol	4.3 ± 0.4	8.7	$^{\bullet}C_4H_2N_2O_2^-$	C_2H_5OH
bromouracil + 10 mmol dm^{-3} ethanoate + ethanol	5.8 ± 0.4	7	$^{\bullet}C_4H_3N_2O_2$	C_2H_5OH
bromouracil + methanoate	373 ± 2	7	$^{\bullet}C_4H_3N_2O_2$	$HCOO^-$
4-iodophenol + 10 mmol dm^{-3} hydrogen carbonate + ethanol	141 ± 3	7	$^{\bullet}C_6H_4OH$	C_2H_5OH
4-iodophenol + 10 mmol dm^{-3} hydrogen carbonate + methanol	5.9 ± 0.8	7	$^{\bullet}C_6H_4OH$	CH_3OH
4-iodophenol + methanoate	2050 ± 80	7	$^{\bullet}C_6H_4OH$	$HCOO^-$
3-iodophenol + methanoate	2000 ± 200	7	$^{\bullet}C_6H_4OH$	$HCOO^-$
2-iodophenol + methanoate	4600 ± 300	7	$^{\bullet}C_6H_4OH$	$HCOO^-$